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TITLE   CRITICAL REACTION RATES IN HYPERSONIC COMBUSTION CHEMISTRY

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CRITICAL REACTION RATES
IN HYPERSONIC COMBUSTION CHEMISTRY

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INTRODUCTION:

High Mach number flight requires that the scramjet propulsion system operate at a relatively low static inlet pressure and a high inlet temperature. These two constraints can lead to extremely high temperatures in the combustor, yielding high densities of radical species and correspondingly poor chemical combustion efficiency. As the temperature drops in the nozzle expansion, recombination of these excess radicals can produce more product species, higher heat yield, and potentially more thrust. The extent to which the chemical efficiency can be enhanced in the nozzle expansion depends directly on the rate of the radical recombination reactions.

Radical recombination reactions rely on collisions to stabilize products, and consequently the rates of these reactions are, in general, pressure dependent. The low pressures inherent in high Mach number, high altitude flight can, therefore, slow these reaction rates significantly, relative to their rates in more conventional propulsion systems. This slowing of the chemistry is further compounded because high Mach number flight also implies high internal velocities that result in very short residence times (millisecond time range) in a hypersonic engine. Consequently, the finite rates of these chemical reactions may be a limiting factor in the extraction of the available chemical energy. A comprehensive assessment of the important chemical processes and an experimental validation of the critical rate parameters is therefore required if accurate predictions of scramjet performance are to be obtained

IDENTIFICATION OF CRITICAL REACTIONS,

A chemical kinetics computer simulation code has been employed for modeling the hydrogen/air combustion in a basic hypersonic ramjet engine design The code
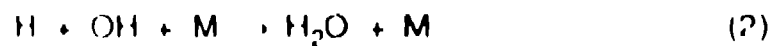
models the kinetics and thermomechanics of premixed, quasi-one dimensional, time-steady streamline segments. Details of the calculations and the reaction rate constants employed are presented elsewhere [1]. The code is far simpler than conventional CFD codes, and does not consider the effects of mixing, conduction, convection, or diffusion. Our motivation is not to accurately predict scramjet performance, but to assess the role of finite-rate chemistry in the combustion process and to identify key rate-limiting steps in the combustion process.

Using this code, comparisons were made, for a variety of engine designs and flight conditions, between calculations involving finite-rate chemistry and those in which equilibrium conditions are maintained. In particular, radical densities and the energy yield, i.e., the fraction of the maximum possible heat of combustion achieved, were examined. From these comparisons, we find that the use of finite-rate chemistry models in the combustor section has only a minimal effect on the predicted performance. In contrast, very large differences are observed in the nozzle expansion, driven by the rapid drop in pressure and temperature. The finite-rate chemistry model predicts significantly higher radical concentrations at the nozzle exit, with a corresponding decrease in energy yield.

A sensitivity analysis of the chemical reaction model was conducted to identify which reactions are the key rate-limiting steps in the heat release mechanism during the nozzle expansion. Most of the bimolecular reactions, such as

$$OH + H_2 \leftrightarrow H + H_2O \qquad (1).$$

were found to be very fast under typical scramjet operating conditions and tend to reach a partial equilibrium. Consequently, the exact magnitude of the bimolecular reaction rate constants that are involved should have little impact on the overall chemistry. In contrast, four termolecular radical recombination reactions were found to be particularly rate- and, therefore, performance-limiting. These critical limiting reactions are:

$$H + OH + M \rightarrow H_2O + M \qquad (2)$$

$$H + H + M \rightarrow H_2 + M \qquad (3)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (4)$$

$$H + O + M \rightarrow OH + M \qquad\qquad (5).$$

The important collision partners, collectively denoted as M in the above expressions, are H_2O, N_2, H_2, and possible H-atoms under typical hypersonic combustion conditions. The relative importance of these four reactions varies with equivalence ratio. All tend to be significant under stoichiometric conditions. As might be expected, the importance of reaction (3) decreases in fuel lean conditions, while reactions (4) and (5) decrease in fuel rich conditions.

The exact rate constants for these selected reactions that are used in the simulations can dramatically affect predicted combustion efficiency and engine performance. It is therefore of critical importance that the rate constants for these reactions be well determined if accurate predictions of scramjet performance are to be obtained.

The accuracy to which the rate constants for these processes are presently known was examined. Figure 1 summarizes the published data acquired over the past half century for reaction (2), where M = H_2O. For references to the original studies from which these data were obtained, refer to the Leeds compilation [2]. The data in figure 1 fall into two groups, high temperature measurements around 2000K from flame and shock tube experiments, and room temperature data from flash photolysis experiments. The span in the rate constant data at either temperature is nearly two orders of-magnitude. The solid line in the figure is the recommended value of Baulch et al [2], but clearly the large spread in the data on which this recommendation is based reveals the unacceptably large uncertainties inherent in this value, as noted in the original compilation. Examination of the data for reaction (2) with other collision partners, M, as well as the data for reactions (3), (4), and (5) show similar uncertainties. The critical importance of these recombination reactions to nozzle performance, combined with the large unacceptable scatter in the literature data, indicate that these reactions are prime candidates for experimental study.

EXPERIMENTAL MEASUREMENTS:

The rate constants for reactions identified through the modeling simulations as critical for good scramjet performance are being experimentally determined using the laser photolysis / laser induced fluorescence (LP/LIF) relaxation kinetics technique. In this technique, water vapor, containing various added amounts of hydrogen, oxygen, and/or nitrogen, is equilibrated at temperatures extending from room temperature to 1800K (3200R) and at total pressures in the range 7 - 30 psia. This equilibrium mixture will be perturbed essentially instantaneously using excimer laser photolysis to
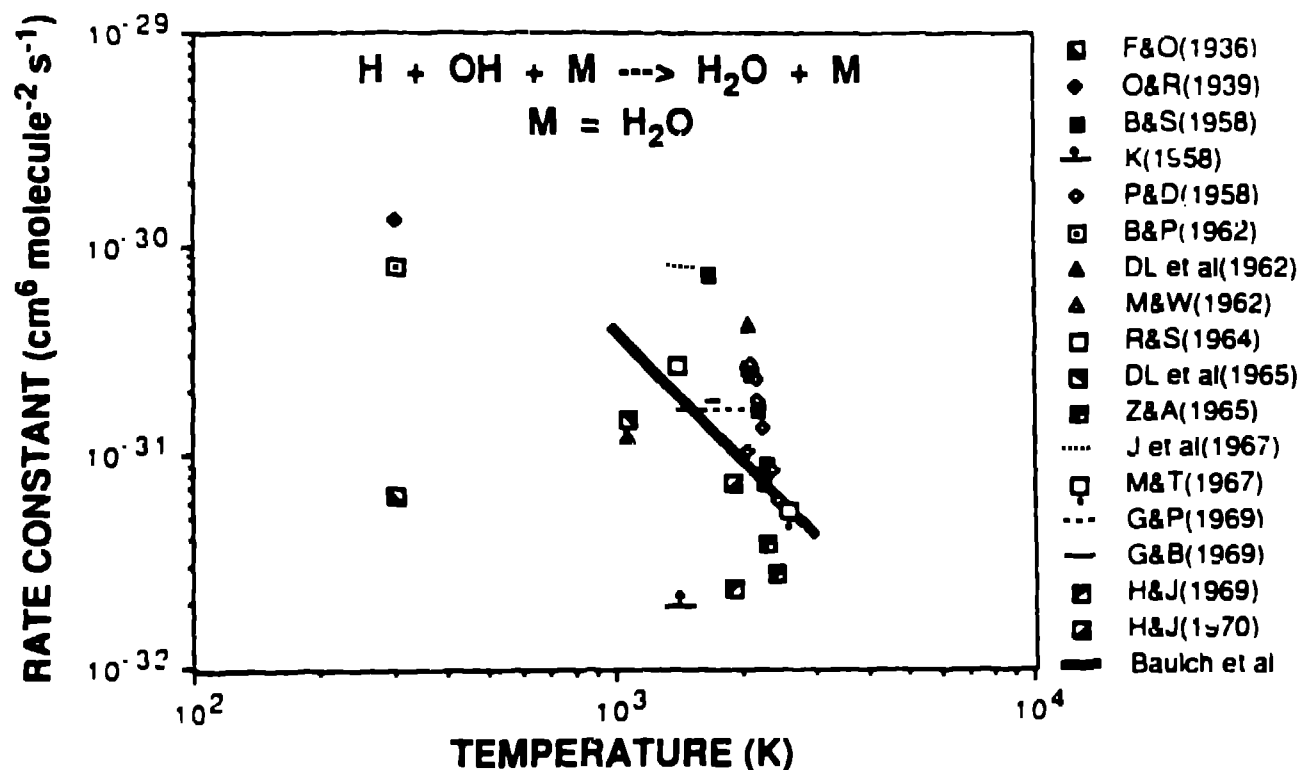
Figure 1. Summary of published rate constant data for H + OH + M reaction

as to increase the concentrations of the OH radicals and H atoms by

$$H_2O + h\nu(193nm) \rightarrow OH + H \qquad (6)$$

The absolute densities of the photolytically introduced radicals can be determined from the laser fluence and an independently determined photodissociation cross section for water vapor. Laser-induced fluorescence is then used to monitor the subsequent time histories of the OH and/or H as they return to their equilibrium concentration. The time required for the chemical system to return to equilibrium, i.e., the relaxation time, is measured and compared to predictions of the chemical kinetic modeling code under identical conditions. Since this technique simultaneously evaluates the entire relaxation mechanism, we can be assured that all key reactions are addressed in the experiment and that a self-consistent set of rate constants can be obtained

Before beginning the recombination rate constant measurements, direct measure

ments of the rate constant of the bimolecular reaction

$$OH + H_2 \rightarrow H + H_2O \qquad\qquad (1a)$$

were completed in the temperature range 800-1550K. The OH is removed by this reaction as the partial equilibration of the OH and H-atom densities is attained. Analysis of the fast OH removal rates as a function of added hydrogen yields the rate constant for the above reaction.

The rate constant for this reaction has been well determined in a number of previous studies by other workers and was recently reexamined by Michael and Sutherland [3]. They combined their shock tube data with those of Frank and Just and the flash photolysis data of Tully, Ravishankara, and co-workers, and derived the expression:

$$k = 3.59 \times 10^{16} T^{1.51} exp[-1726 / T] \ cm^3 molecule^{-1}s^{-1} ,$$

which is applicable in the temperature range 250-2581 K. Our recent measurements bridge the gap between the shock tube data (1246-2581 K) and the flash photolysis data (250-1050 K) and are in very good agreement with these previous data sets in the overlap region. Our data points lie slightly above the fit expression recommended by Michael and Sutherland. We combined our data with the three data sets they used and the recently reported data [4] of Davidson, Chang, and Hanson, to derive a new expression for the rate constant:

$$k = 3.56 \times 10^{16} T^{1.52} exp[-1736 / T] \ cm^3 molecule^{-1}s^{-1} .$$

The constants in this expression are nearly identical to those in the Michael and Sutherland expression. However, the rate constants calculated with this new expression are a few percent higher, averaged over the entire temperature range. Figure 2 shows an Arrhenius plot of our recently obtained data (LANL) along with some of the other data values obtained from published papers and used in determining the fit expression. The fit line shown in the figure is based on our recommended expression. These results are presently being prepared for publication.

The purpose of these measurements was to validate the kinetic measurement techniques employed in these experiments by reevaluating a well known rate constant, in preparation for our recombination rate constant measurements. Having achieved this objective, our studies have begun on the recombination reactions.
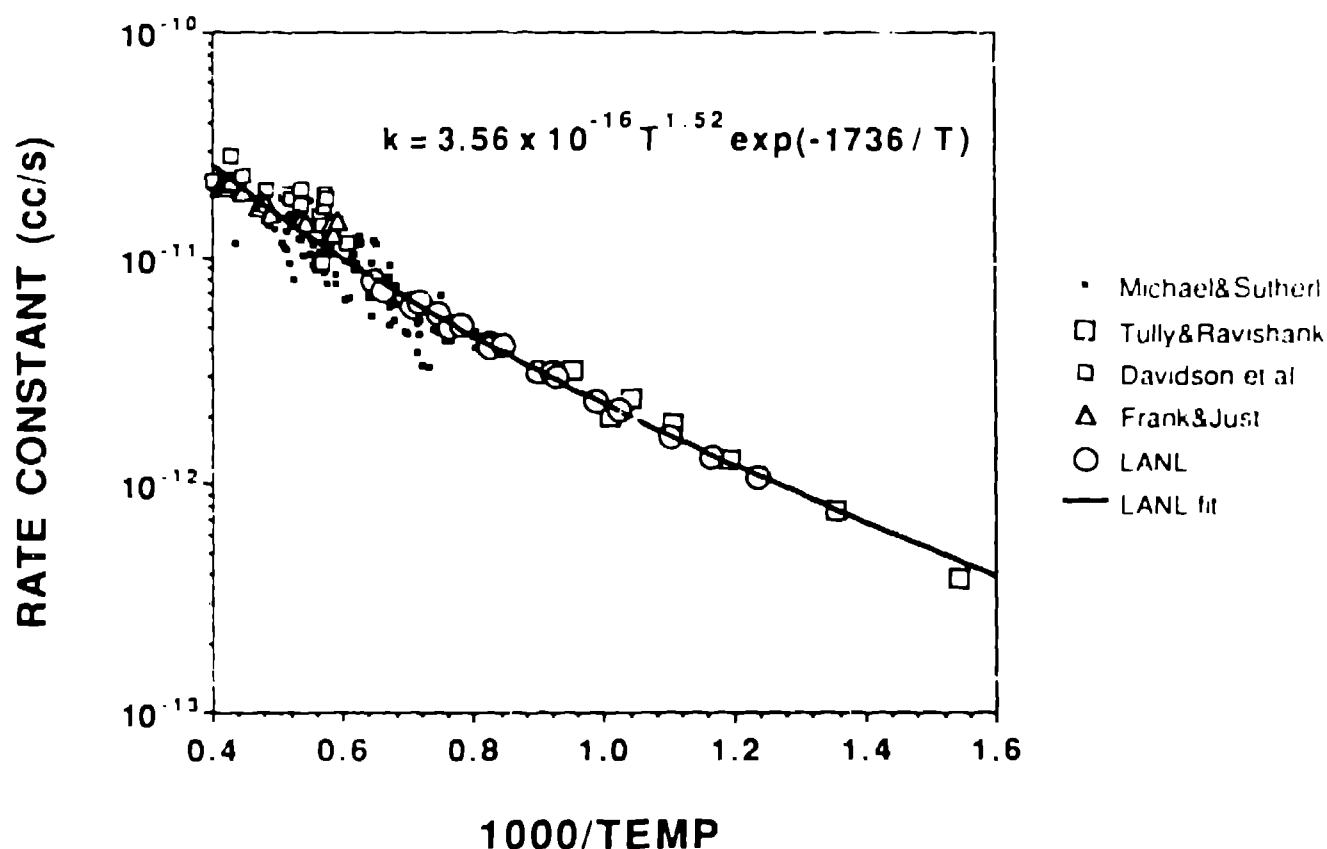
Figure 2. Arrhenius plot of rate constant data for OH + H$_2$ → H + H$_2$O reaction

Preliminary rate constant values for recombination reactions (2) and (3) have now been obtained at a single temperature (1223 K). However, the uncertainty of these measurements is at present unacceptably large. Relaxation rate measurements at this temperature for additional gas compositions are in progress. Variation of the gas composition allows different reactions to dominate the chemistry, and consequently this additional data should improve the precision of these rate constant determinations. Over the next few months, the temperature range of these measurements will be extended to the limits of our present high temperature cell (300 - 1800 K). The wide temperature range of these experiments (note Fig. 1) should allow accurate extrapolations of these new rate constants into temperature regimes of relevance for hypersonic combustion. The status of these measurements will be discussed in the presentation.

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